Crystalline β-$Co(OH)_2$ Thin Films as an Electrode material for Electrochemical Capacitor Application

[1]Sanjay L. Gaikwad, [3]Ankita P. Angre, [1]Abhishek Suryawanshi, [2]Purushottam R. Arjunwadkar, [1,2]Paresh S. Gaikar*

[1] Mahatma Phule A. S. C. College, Panvel, Raigad, 410206, India

[2] Department of Physics, Institute of Science, Nagpur, 440008, India.

[3]Satish Pradhan Dnyanasadhana College, Thane, 400064, India

Abstract -Wide application and properties in transition metal oxides and hydroxides, Cobalt hydroxide ($Co(OH)_2$) has recently received substantial attention due to its distinctive catalytic, electric, magnetic and electrochemical supercapacitive properties for industrial applications. The nano-rhombus like β-$Co(OH)_2$ thin films were successfully synthesized onto a stainless steel substrate by a simple, versatile and economical chemical bath deposition (CBD) method. The crystal structure and morphology of the β-$Co(OH)_2$ thin films were explored by X-ray diffraction (XRD) & scanning electron microscopy (SEM) techniques respectively. The supercapacitive properties of nanorhombus-like β-$Co(OH)_2$ thin films were evaluated in 1M KOH aqueous electrolyte by using cyclic voltammetry & galvanostatic charge-discharge method. The nano-rhombus like β-$Co(OH)_2$ thin films were shown exceptional specific capacitance 280 F g^{-1} at 2 mV s^{-1} with 64% retention up to 30 mV s^{-1} by cyclic voltammetry measurement as well as maximum specific capacitance 242 F g^{-1} at 1 mA cm^{-2} with 66% retention up to 10 mA cm^{-2} by galvanostatic charge-discharge measurement. Present investigation proposes that the high surface morphology of nanorhombus like structure makes β-$Co(OH)_2$ as highly effective materials for energy storage applications.

Keyword- Cobalt hydroxide, Electrochemical Capacitor, Scanning electron microscopy, Cyclic voltammetry, Galvanostatic charge-discharge measurement.

1. Introduction-

Increasingly fierce climate change, depletion of fossil fuels and growing environmental pollution are driving human beings to find sustainable and renewable resources as well as new technologies associated with energy conversion and storage[1-2]. Amongst the energy storage devices, supercapacitors have fascinated more attention as a promising energy storage device because of their properties like high power density, long cycle. Furthermore, the power and energy gaps between batteries and second conventional stability, higher specific capacitance and short charging-discharging time etc. [3] capacitors fulfilled by supercapacitors, which is also known as electrochemical capacitors, it has significant potential for energy storage and electric vehicles. Electrochemical capacitors can be categorized mainly into carbon-based materials, [4] conducting polymers [5] and transitional metal compounds [6]. Transitional metal compounds have features like high surface area, rich redox chemistry and short electron and ion transport pathways, which renders its potential use for the next generation of electrochemical capacitors [7]. Extreme work on electrochemical capacitors utilizing pseudocapacitance has motivated on metal hydroxide and oxide materials. Initially, RuO_2 generated great interest due to its extraordinary specific capacitance with reversibility [8-9], however, the expensiveness of RuO_2 and the toxicity associated with the use of strong acidic electrolytes have limited its commercial use [9]. Therefore, the development of alternative cheap electrode materials with great performance has been one of the most dynamic research areas of a supercapacitor in the last few years. So $Co(OH)_2$ has characteristics like environmentally friendly in nature, cost-effective, outstanding electrochemical activity, high theoretical specific capacitance, it has been recommended [10-12]. In the synthesis of chemical methods, Chemical Bath Deposition (CBD) has its individual advantages such as simplicity, inexpensiveness, reproducibility. This method is low temperature and does not need sophisticated instruments [13-14]. In the present investigation, CBD was employed for the synthesis of nanorhombus-like of $Co(OH)_2$ morphologies. Further, a thin film used for Structural and morphological studies and electrochemical properties.

2. Experimental details

2.1 Chemicals

Cobalt acetate, Urea, and Ammonium fluoride were of analytical grade and used without further purification. All syntheses were carried out in triply distilled water.

2.2 Synthesis of $Co(OH)_2$

$Co(OH)_2$ of nanorhombus-like morphologies was effectively synthesized by CBD method by following the procedure as; 0.1 M of Cobalt acetate, 0.5 M Urea and 0.2 M Ammonium fluoride were dissolved in 50 ml of distilled water under magnetic stirring for 1 hour. The obtained pink solution was transferred into falcon tubes. Stainless steel immersed falcon tubes were sealed and kept in a water bath at 90^{o} C for 20 hrs. After completion of the reaction, light pink color β-$Co(OH)_2$ films were obtained. The obtained films were washed with water. Afterward, as a synthesized nanorhombus-like $Co(OH)_2$ films are used for further characterization.

2.3 Material Characterization

The structural identification of synthesized β-$Co(OH)_2$ thin film was carried out using X-ray diffractometer with CuKα source (λ=0.154 nm). Surface morphologies of films were studied using scanning electron microscopy (SEM). All the electrochemical experiments were carried out in 1 M KOH aqueous electrolyte at room temperature using Ivumstat. Cyclic voltammetry (CV), Galvanostatic Charge-Discharge (GCD) carried out in a standard three-electrode system with a saturated Ag/AgCl electrode and platinum as the reference electrodes and counter electrode respectively.

3 Results and Discussion

3.1 Structural analysis

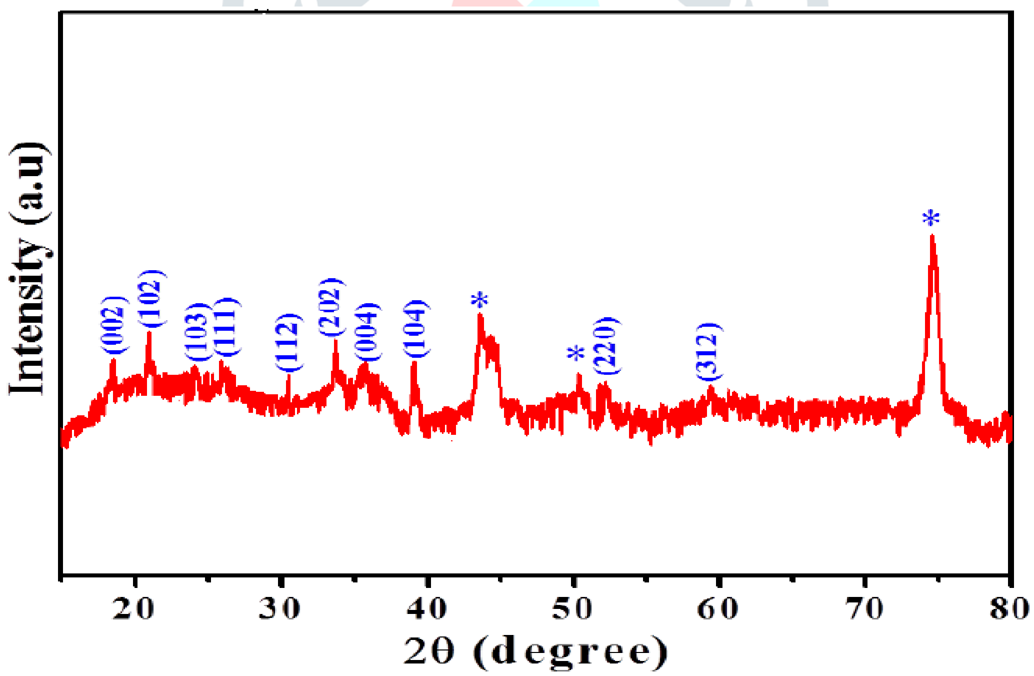

Fig.1 XRD pattern of β- $Co(OH)_2$ thin films

Fig.1 shows the XRD pattern of an as-deposited $Co(OH)_2$ film on a stainless steel substrate. The XRD pattern of $Co(OH)_2$ thin film shown number of reflections along with the (002), (102), (111), (103), (112), (202), (004), (104), (220) and (312) planes respectively, which is confirming the polycrystalline nature of as-prepared β- $Co(OH)_2$ samples according to the standard JCPDS file No. 45-0031 which communicate with structure, and '*' symbol displayed the peaks of the stainless steel substrate. No other impurity peaks found in the XRD pattern which confirmed that the stoichiometric purity of the β-$Co(OH)_2$ samples. The average crystallite size of the samples was calculated using the following famous Debye-Scherrer relation;

$$D = \frac{\alpha * \lambda}{\beta * \cos\theta} \qquad (1)$$

where ‘D’ is crystallite size, ‘α’ is a geometrical factor (equal to 0.94), ‘λ’ is the wavelength (1.5406Å), ‘β’ is the half-width of diffraction peak and ‘θ’ is the angle of the diffraction. Average crystallite size for β-$Co(OH)_2$ samples were found to be 23.84 nm.

3.2 Morphological Evolution

Fig.2 shows low and high magnification scanning electron microscope images of $Co(OH)_2$ thin films which demonstrate that the nanorhombus like morphology. The stacked nanorhombus with regular size is grown from the bottom and it also has air voids. So this characteristic of nanorhombus like morphology will be helpful $Co(OH)_2$ to be the good candidate for electrochemical supercapacitor application.

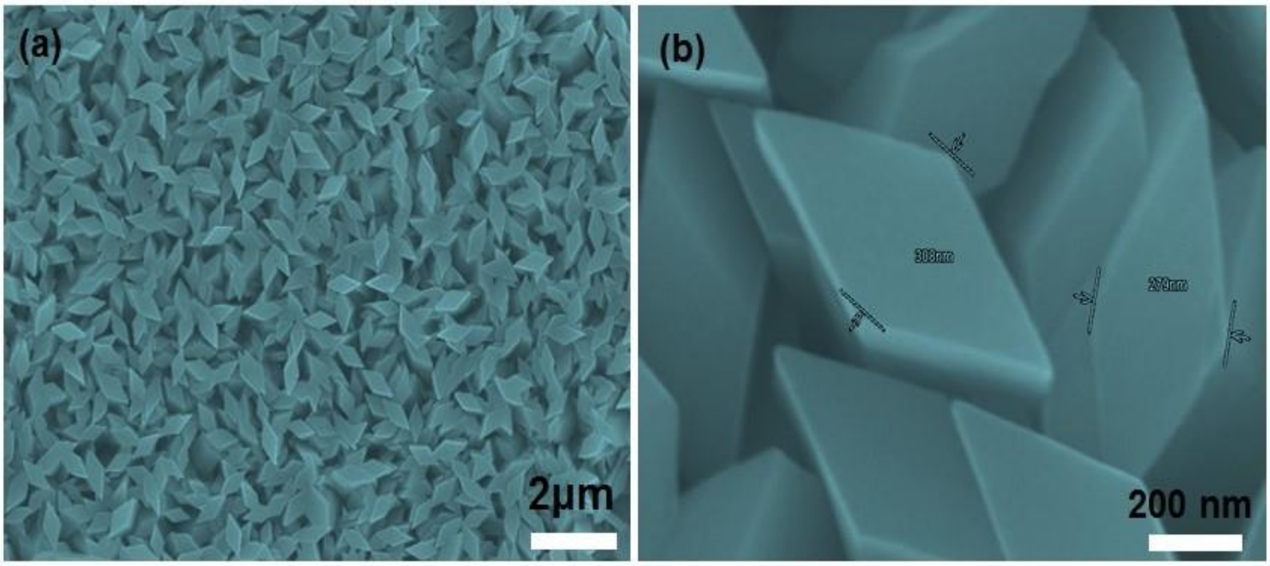

Fig. 2 (a) Low magnification (b) High magnification SEM images of the β-$Co(OH)_2$ thin films

4. Electrochemical measurements

4. 1 Cyclic-voltammetry

The supercapacitive performance of $Co(OH)_2$ electrode material was carried out by cyclic-voltammetry and charge-discharging measurements. Specific capacitance (SC) is one of the vital indices for estimation of electrochemical performance which was calculated according to relation;

$$SC= \frac{I}{m\frac{dV}{dt}} \qquad (2)$$

Where, ‘I’ is the current in ampere, ‘m’ is the mass of the electro-active material in grams and $\frac{dV}{dt}$ is scan rate in mV s^{-1} . Fig. 3a) presents the typical CV curves of $Co(OH)_2$ electrode at various scan rates of 2-30 mVs^{-1} in the potential window ranging from 0.0 to 5.5 V (vs. Ag/AgCl). A non-rectangular form of cyclic voltammogram is due to the pseudocapacitive contribution of the film [14]. The CV pattern showed that as the scan rate increases the area under the curve of the electrode increases. The maximum specific capacitance is found that 280 F g^{-1} at 2 mVs^{-1} scan rate. We found that 64% retention of the specific capacitance value after 30 mVs^{-1} scan rate. The fig. (3b) demonstrated that as the scan rate increases the specific capacitance decreases. It's because of the existence of internal active sites, which normally are not involved in the redox reactions completely [15].

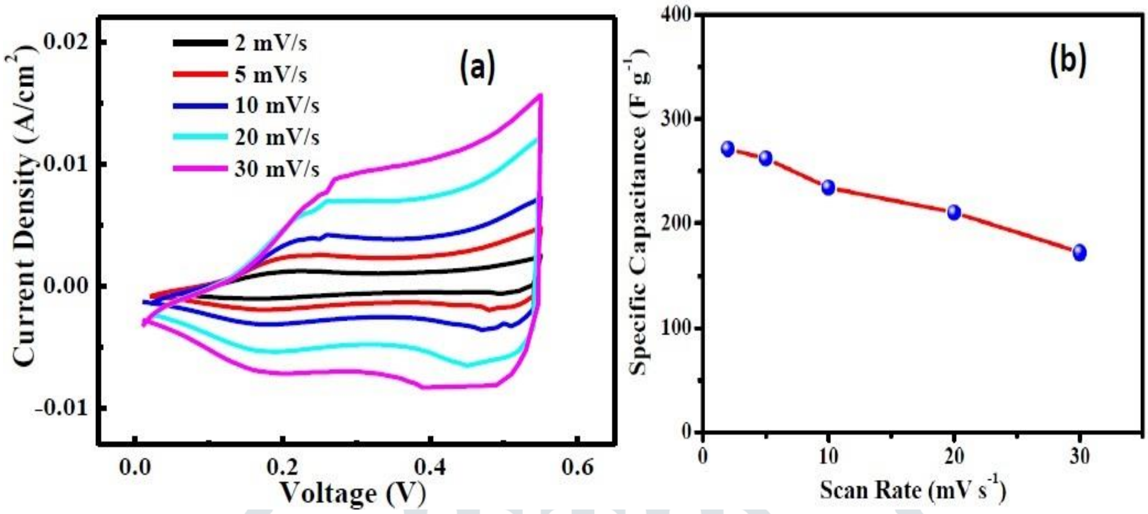

Fig.3. (a) Cyclic Voltammetry measurement recorded at a scan rate of 2, 5,10 ,20 and 30 mV s^{-1}, (b) plot of the effect of scan rate on the Specific Capacitance value of β- $Co(OH)_2$ electrode

4.2 Galvanometric charge-discharge measurement

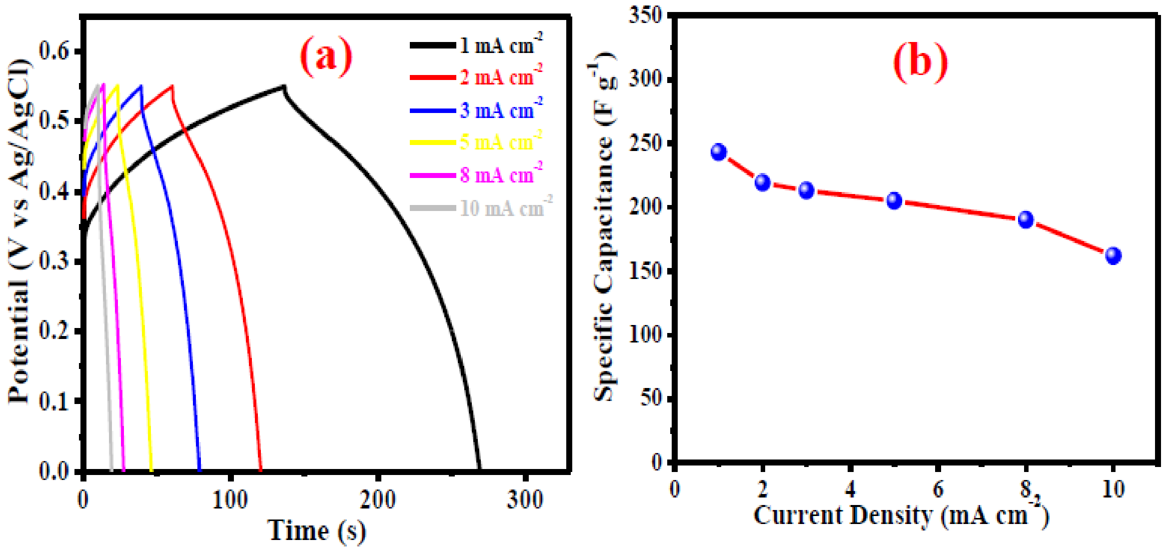

Fig.4. (a) Galvanometric charge-discharge measurement recorded at a current density of 1, 2, 3, 5, 8 and 10 mA cm^{-2}, (b) plot of the effect of current density on the Specific Capacitance value of β-$Co(OH)_2$ electrode

The galvanostatic charge discharge (GCD) curves of β-$Co(OH)_2$ (Fig. 4(a)) electrode at different current densities of 1-10 mA cm^{-2} which show that the as the current density decreases the discharge time increases, demonstrating relatively higher specific capacitance at 1 mA cm^{-2}. Specific capacitance values by using GCD curves were also calculated using the following equation:

$$SC = \frac{i * T_d}{m * \Delta V} \qquad (3)$$

where 'i' is the discharge current in amperes, 'T_d' is the discharge time in seconds, 'm' is the mass of the electro-active material in grams and 'ΔV' is the potential window for the calculated SC of β-$Co(OH)_2$ electrode in 1M KOH electrolyte are 242, 219, 213,205, 190 and 162 F g^{-1} obtained at current densities of 1, 2, 3,5.8 and 10 mA cm^{-2}, respectively. Fig. 4(b) shows the plot of specific capacitance with varying current densities for β-$Co(OH)_2$ electrode. β-$Co(OH)_2$ electrode demonstrate that 66% retention of specific capacitance after the current density 10 mA cm^{-2}.

5. Conclusion

In a summary, this works demonstrates a simple and cost-effective chemical bath deposition method for the synthesis of nanorhombus β-$Co(OH)_2$ on a stainless steel substrate. Cyclic Voltammetry study of β-$Co(OH)_2$ electrode shown exceptional specific capacitance 280 F g^{-1} at 2 mV s^{-1} with 64% retention up to 30 mV s^{-1} as well galvanostatic charge-discharge measurement shown maximum specific capacitance 242 F g^{-1} at 1 mA cm^{-2} with 66% retention up to 10 mA cm^{-2}.

6. References

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